

FINAL REPORT
Electroactive Polymeric Materials for Supercapacitors
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TECHNICAL OBJECTIVES

This program was directed to the use of conjugated and highly electroactive polymers (EAPs) as the active redox materials in electrochemical supercapacitors (SCs). This report summarizes the results that have been obtained between April 2014 and April 2017. We have aimed to take advantage of a major benefit of conjugated electroactive polymers, which is their ability to be room temperature solution processed using roll-to-roll compatible coating methods onto lightweight, flexible substrates of various shapes and sizes. We proposed to (i) develop a family of solution processable dioxothiophene (XDOT) polymers that are easily oxidized and have a broad pseudocapacitive response, (ii) develop soluble polymers that are compatible with aqueous electrolytes using either polar side chains or tethered ionic functionalities, (iii) define structure-property relationships that determine charge storage capacity, discharge rates, and polymer/substrate and polymer/electrolyte interactions, and (iv) incorporate the optimized polymers into various composites either using transition metal oxides or different 3D carbon structures to maximize the pseudocapacitance.

TECHNICAL APPROACH

Our general approach was to focus on synthesizing electron-rich polymers that can be reversibly and rapidly (< 2 sec) charged/discharged between the oxidized (conducting) and neutral (non-conducting) states and incorporated into Type I and/or Type II SCs. Our earlier work showed that electrochemically polymerized dioxothiophene-based EAPs are highly stable over 10^5 - 10^6 charge/discharge cycles and can easily be constructed into thin layer modules for increasing the device current or device voltage.^{1,2,3} Over this grant period, our primary goal was to develop a family of pseudocapacitive polymers with a similar design motif, but that also incorporates solubilizing repeat units so that the final material is not only electroactive over a broad voltage range but also soluble in a variety of solvents (organic and aqueous). These optimized structures have then been incorporated into both 2D devices as well as into various high surface area carbon materials. Our general approach is highlighted in **Figure 1**.

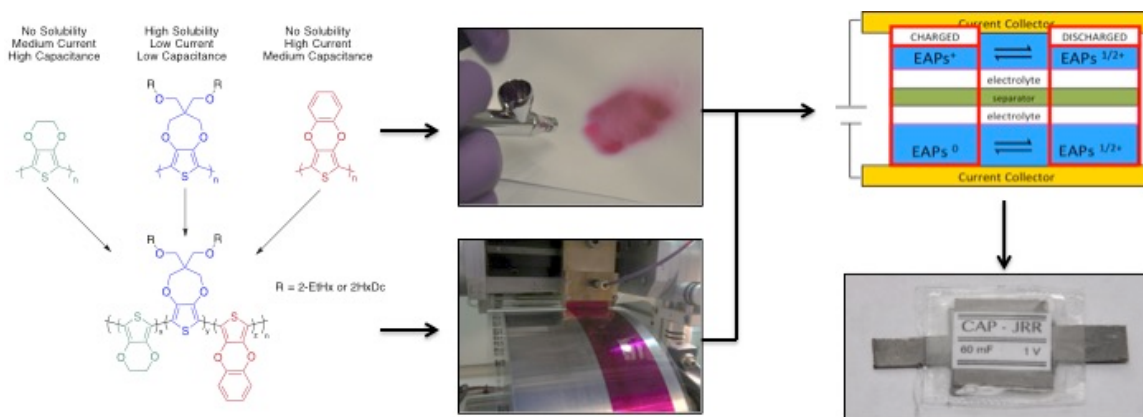


Figure 1. Design approach for developing soluble, pseudocapacitive copolymers (left) that can be processed via high-throughput coating methods (middle), and incorporated into thin and flexible Type I/II devices (right).

PROGRESS SUMMARY

The main challenge for developing soluble polymers for supercapacitors is that most conjugated homopolymers with a narrow polydispersity are electroactive in a very narrow voltage window usually spanning less than 1 V. Previously, attempts have been made to develop a soluble version of poly(3,4-ethylenedioxythiophene) (PEDOT, rightmost structure in **Figure 2**) by functionalization of the ethylene bridge with alkyl chains, but any direct manipulation of the EDOT unit changes the redox properties and drastically increases the onset of oxidation of the resulting polymer as a result of the increased steric bulk and regioirregularity induced by the solubilizing groups. Our first generation of soluble XDOTs (see structures in **Figure 2**) was made by copolymerizing various ratios of unfunctionalized EDOT with alkoxy-functionalized 3,4-propylenedioxythiophene (ProDOT) as the solubilizing unit using direct arylation polymerization (DHAP).⁴ In this first study, we were able to show that these copolymers are electrochemically similar or even equivalent to PEDOT with the added benefit of being highly soluble in organic solvents without having to structurally modify the EDOT unit or use any additional surfactants or dispersants. By increasing the number of EDOT units in the repeat unit we were able to lower the onset of oxidation without compromising the broad redox response as shown in **Figure 3**.

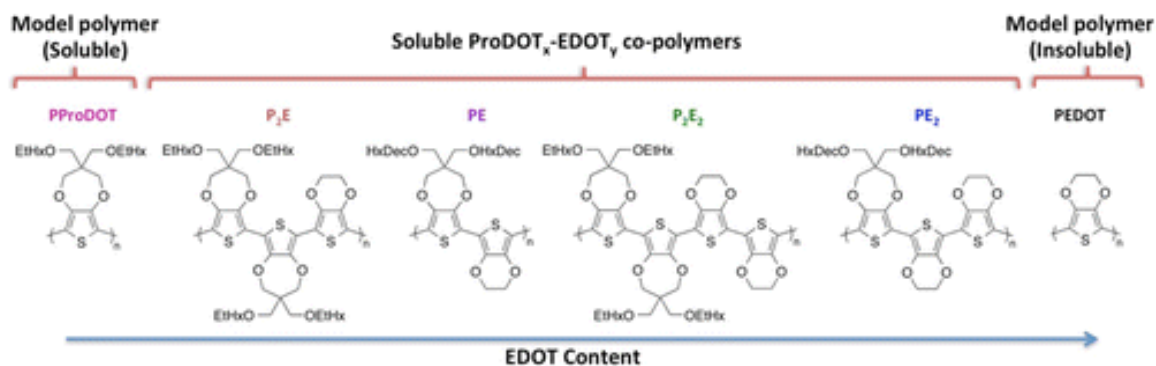


Figure 2. Full series of ProDOT_x-EDOT_y (P_xE_y) copolymers as well as the parent homopolymers. Taken from reference 4.

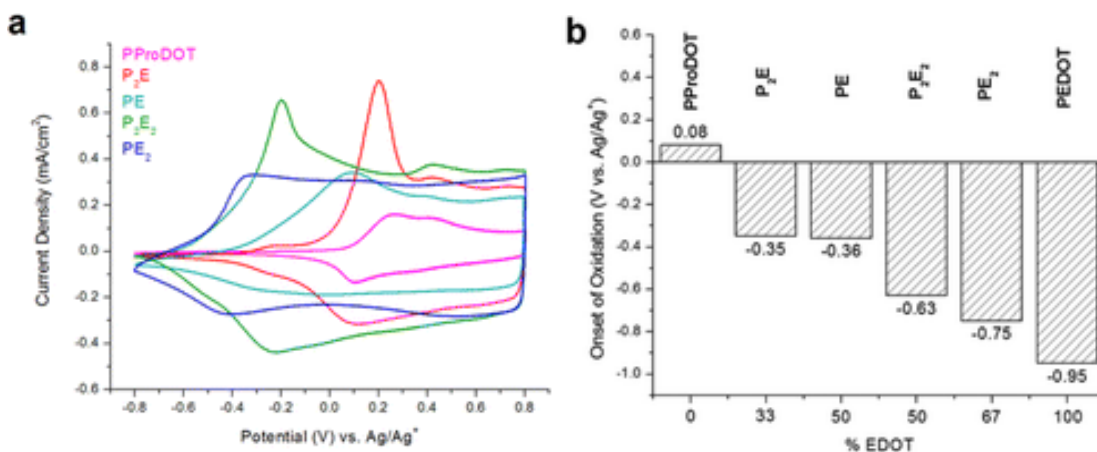


Figure 3. a) Cyclic voltammograms of PProDOT and the P_xE_y copolymers at 50 mV/s b) onset of oxidation determined by differential pulse voltammetry as a function of EDOT content in P_xE_y copolymers compared to their parent polymers PProDOT and PEDOT. Taken from reference 4.

Based on these results, we evaluated PProDOT₂-EDOT₂ and PProDOT-EDOT₂ in 2D Type I devices.⁵ Supercapacitors incorporating these polymers achieved voltages up to 1.6 V (**Figure 4a**), outperforming most Type I and Type II polymer-based supercapacitors. In addition, they exhibit energy densities (4–18 Wh/kg depending on the voltage) and power densities (0.8–3.3 kW/kg) that are comparable or superior to those measured for supercapacitors incorporating electrochemically polymerized PXDOTs and PXDOPs and promise long-term stability with minimal capacitance loss even after 50,000 cycles (**Figure 4b**).

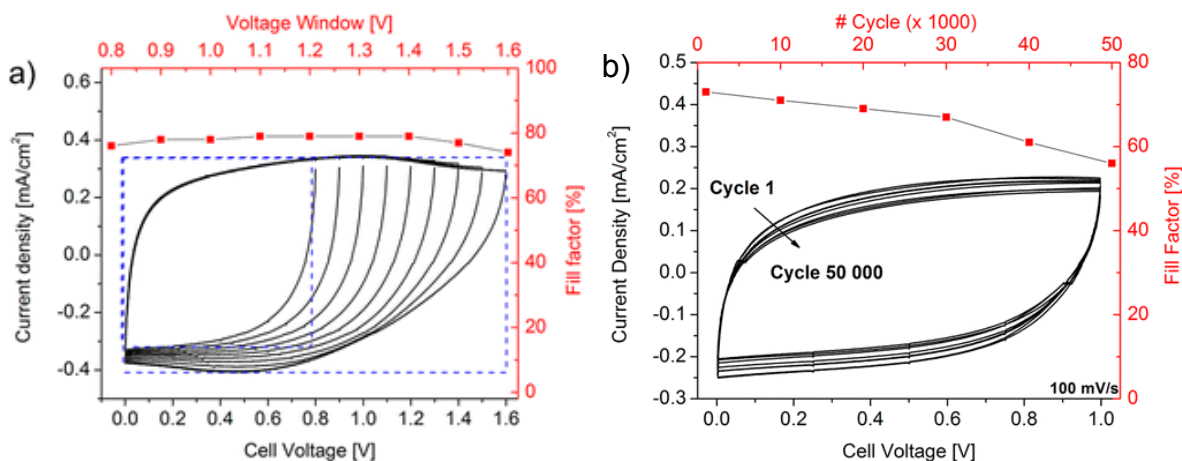


Figure 4. a) Effect on fill factor and redox behavior a PProDOT-EDOT₂ supercapacitors with increased cell voltage at 50 mV/s, b) Cycling stability and fill factor retention of a PE₂ device over the course of 50 000 cycles. Taken from reference 5.

In an attempt to improve the rate capability and capacitance, we synthesized another family of soluble copolymers where the capacitive EDOT units were replaced with planar PheDOT units to promote π -stacking interactions between chains and boost the current. These new copolymers were also synthesized using direct arylation polymerization according to the scheme in **Figure 5**, of alkoxyfunctionalized PProDOT as the solubilizing unit with either PheDOT or biPheDOT. The incorporation of PheDOT resulted in copolymers that exhibited 4x higher currents and film capacitance, 0.2 V lower onset of oxidation, and two orders of magnitude higher conductivity than PProDOT, as shown in **Figure 5**. In contrast to what we observed for the P_xE_y family, increasing the PheDOT content from 50 to 67 % did not result in a further increase in current or a lowering of the onset of oxidation. However, because of their higher onset of oxidation they did not outperform the P_xE_y analogues. Although the PheDOT study did not improve the capacitance, it did provide us with structure-property relationships for our design approach; (i) maintaining a high electron density on the DOT unit is more important than maintaining a high degree of planarity between DOT units, (ii) steric interactions between rings should be minimized, and (iii) the large solubilizing side-chains affect the discharge rates. The latter was confirmed by X-ray and thermoanalytical experiments that showed that the incorporation of the solubilizing ProDOT units compromised the solid-state ordering previously observed for the P(PheDOT), compromising the redox currents.

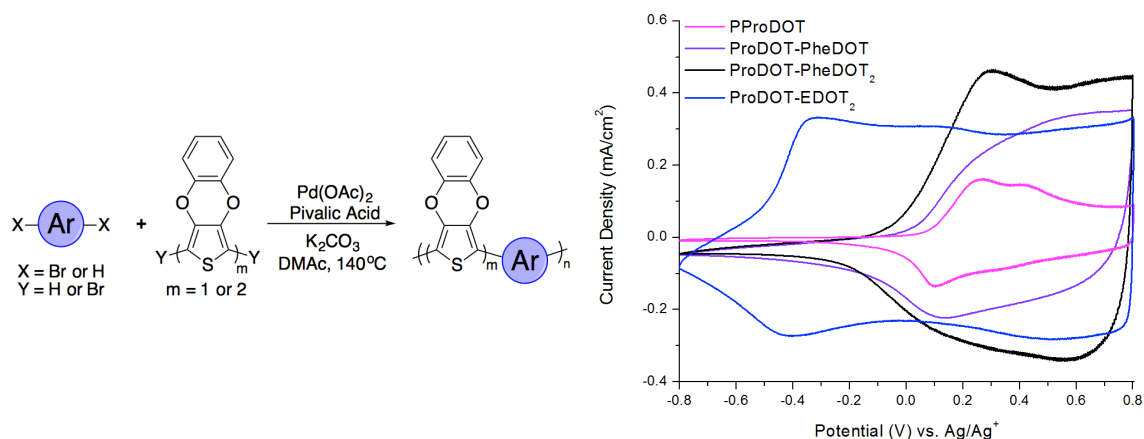


Figure 5. a) Synthetic scheme for ProDOT-PheDOT copolymers, and b) cyclic voltammograms comparing PProDOT, PProDOT-PheDOT, PProDOT-PheDOT₂, and PProDOT-EDOT₂.

In an attempt to expand the device voltage while following these three design principles, we synthesized the first example of a solution processable dioxothiophene-alt-dioxyselenophene copolymer, PProDOT-EDOS, via direct arylation polymerization as shown in **Figure 6**.⁶ By substituting the sulfur atom for a selenium on one of the monomers in the repeat unit an almost 0.2 V reduction in the onset of oxidation is achieved. In addition, PProDOT-EDOS is highly electroactive in a broad potential range (albeit not quite as broad as PProDOT-EDOT as a result of a slightly lower anodic stability) and exhibits similar redox currents as the EDOT analogues. The low onset of oxidation makes these new EDOS-based copolymer very promising materials especially for Type II devices where PProDOT-EDOS can serve as the cathode material and a ProDOT-EDOT₂ as the anode material.

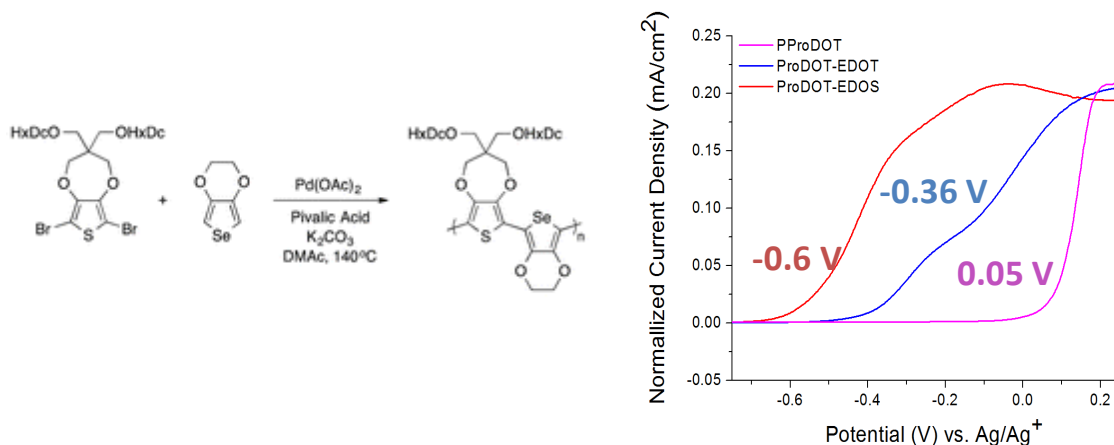


Figure 6. a) Synthetic scheme for ProDOT-EDOS copolymers, and b) cyclic voltammograms comparing PProDOT, PProDOT-EDOS, and PProDOT-EDOT.

To tackle aqueous compatibility and solubility, we have utilized our previously developed method for synthesizing water-soluble electrochromic polymers to create a family of solvent resistant (SR) polymers that are insoluble, while retaining high redox activity, in both organic and aqueous electrolytes. The polymers are synthesized in their ester form and soluble in organic solvents (left structure below), but can be rendered water-soluble through defunctionalization of the alkoxy-chains (middle structure below) with an organic or metal hydroxide. In addition to water, the polyelectrolyte form is highly soluble in other polar solvents such as DMF, but insoluble in non-polar solvents. The water-soluble, polyelectrolyte form can be cast into thin films using a variety of processing methods. The polyelectrolyte films can then be treated with acid to render them solvent resistant (right structure below) making them compatible and with both organic and aqueous electrolyte systems. In addition, these SR polymers are also electroactive in biologically relevant electrolytes such as human serum (blood), Ringer's solution, and urine as well as in commercial sports drinks.⁷

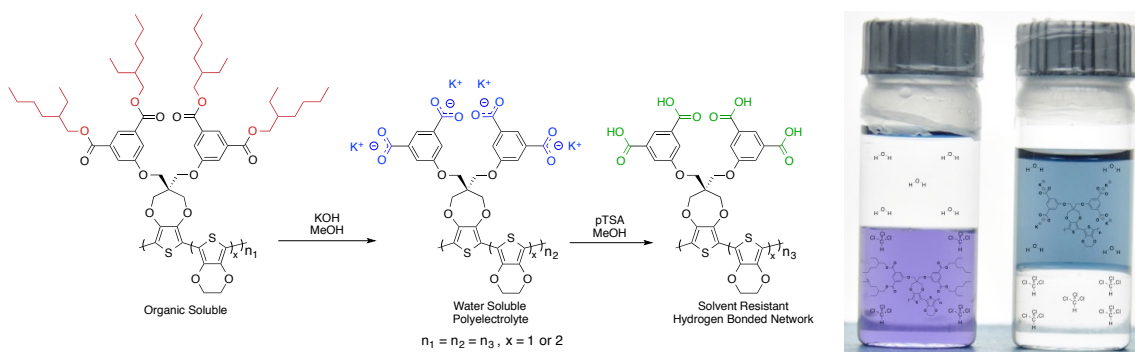


Figure 7. Demonstration of conversion from organic soluble, to water soluble, to solvent resistant form for ProDOT-EDOT (left) and the selective solubility of these polymers in chloroform and water (right).

Devices incorporating solvent resistant ProDOT-EDOT and salt-water exhibit exceptionally fast discharge rates and are able to retain >85% of their capacitance even at 10 V/s corresponding to a discharge time of 0.08 seconds. This is highlighted in **Figure 8a**, where a salt-water device exhibits a perfectly symmetrical charge/discharge curve even at 20 A/g. This demonstrates that these devices have low internal resistance, fast ion diffusion, and fast charge transfer kinetics. The cycling stability of devices incorporating salt-water and assembled under ambient conditions, were monitored over 175,000 charge/discharge cycles at 1 V/s (**Figure 8b**), and these devices are able to maintain >75% of their initial capacitance during these tests. This clearly demonstrates that water does not degrade these PXDOTs over time, and we expect the observed drop in current could be reduced by device preparation under inert atmosphere to remove oxygen from the device.

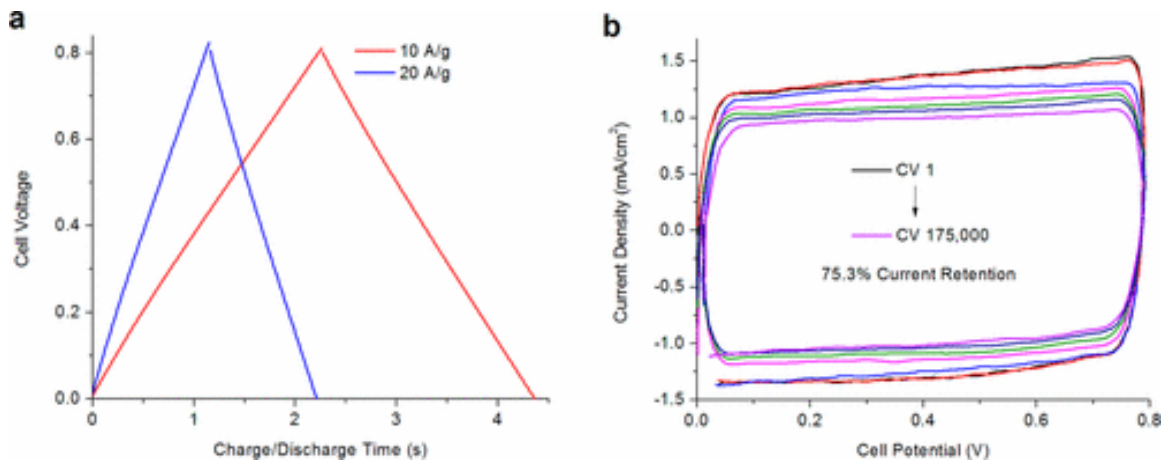


Figure 8. a) Galvanic cycling of a Type I SR-PE supercapacitor using a 0.5 M NaCl/H₂O electrolyte and b) select CVs of an identical device over 175 000 charge/discharge cycles at 1 V/s. Taken from reference 7.

Through a collaboration with the Georgia Tech Research Institute, we had the opportunity to evaluate carbon nanotube (CNT) forest electrodes consisting of densely spaced multi-walled CNTs grown orthogonally on a silicon substrate surface; a schematic representation of these substrates as well as a photograph is shown in **Figure 9**. However, when the CNT substrates were coated with PProDOT-EDOT ink some degree of CNT texturing was observed as a result of CNT aggregation fostered by the introduction of a solvent. While the incorporation of polymer did enhance the capacitance by 100 % compared to the unmodified CNT electrodes, the charge/discharge rate was limited and the substrates were not compatible with roll-to-roll printing/coating.

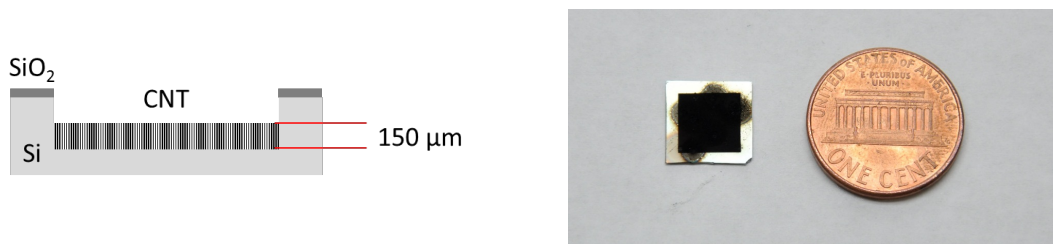


Figure 9. Schematic representation of CNT forest well plate and a photograph of CNT well sample alongside a penny placed for size comparison.

Also produced through a vapor deposition process, non-woven CNT textile (CNT-T) substrates feature a reasonably high surface area, they are highly flexible, and are mass-produced. The addition of 100 wt% of the solvent resistant ProDOT-EDOT₂ to

the CNT-T substrate resulted in a 2x increase in specific mass capacitance and a 4x increase in areal capacitance over the non-functionalized CNT-T using a 0.5 M KCl device electrolyte. These devices exhibit linear scan rate dependence up to 200 mV/s (as shown in **Figure 10a**) and retained 80 % capacity after 10,000 charge/discharge cycles. Mechanical flexibility tests demonstrated that devices could be bent to radii as small as 0.6 mm while retaining their performance. Furthermore, the devices showed total capacity retention after 2000 cycles of repeated flexing to a radius of 3.5mm. The electrode morphology was also characterized by electron microscopy (see **Figure 10b**). For the water-soluble polymer, we found that the vast majority was deposited on the surface of the CNT-T as the hydrophilic ink was not able to permeate the textile. To improve intercalation, we evaluated casting the organic soluble precursor polymer and post treating first with a base and then an acid to attain solvent resistant ProDOT-EDOT₂. While the current response was slightly higher for the device prepared from WS polymer, the difference fit within device-to-device variance. Compared to unmodified CNT-T based devices, both methods produce a capacitance increase of 400% compared to unmodified CNT-T based devices at 20 mV/s where the capacitance is $120 \pm 30 \text{ mF/cm}^3$. Interestingly, despite the differences in SR-PE₂ film morphology, the devices perform identically at increasing charge-discharge rates. Capacitance retention of 59% and 56% at 200 mV/s scan rates is seen for devices based on the WS-PE₂ and OS-PE₂ processing route respectively. This similarity in device performance was a key observation that demonstrated that these solvent resistant polymers are sufficiently conductive for the bulk of a relatively thick, 1 μm film to be as electrochemically accessible a film dispersed throughout the CNT-T.

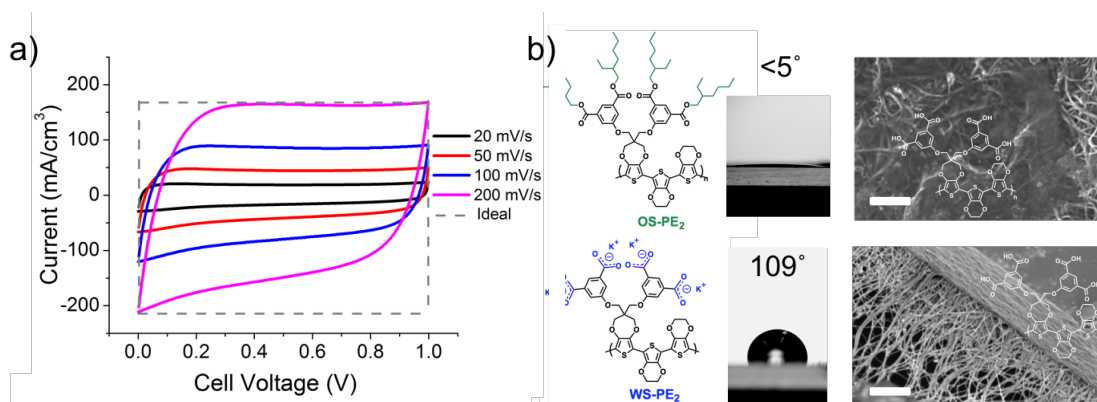


Figure 10. a) Cyclic voltammetry at increasing scan rates for a Type I device incorporating 100 wt% ProDOT-EDOT₂ and 0.5M KCl/H₂O. b) SEM micrograph and contact angle of CNT-T substrate where the polymer has either been cast from chloroform (top images) or water (bottom images).

PUBLICATIONS 2014-2017

Published acknowledging N00014-14-1-0399:

1. Ponder, J. F.; Österholm, A. M.; Reynolds, J. R. *Macromolecules*, 49, 2106-2111 (2016) "Designing Soluble PEDOT Analogs Without Dispersants and Surfactants"
2. Österholm, A. M.; Ponder, J. F.; Kerszulis, J.A.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* 8 13492-13498 (2016) "Soluble PEDOT Analogs in Electrochemical Supercapacitors"
3. Ponder, J. F.; Pitelli, S. L.; Reynolds, J. R. *ACS Macro Lett.* 5, 714-717 (2016) "Heteroatom Role in Polymeric Dioxyselenophene/Dioxythiophene Systems for Color and Redox Control"
4. Ponder, J.F.; Österholm, A. M.; Reynolds, J. R. *Chem. Mater.* "Conjugated Polyelectrolytes as Water Processable Precursors to Aqueous Compatible Redox Active Polymers for Diverse Applications: Electrochromism, Charge Storage, and Biocompatible Organic Electronics"

To be submitted:

1. Lang, A. W.; Ponder, J. F.; Österholm, A. M.; Kennard, N. J. J.; Bulloch, R. H.; Reynolds, J. R. to be submitted to *J. Mater. Chem. A* in 06/2017 "Water-processable dioxothiophene copolymers blended with carbon nanotube textiles for flexible electrochemical supercapacitors"
 2. Ponder, J.F.; Schmatz, B.; Hernandez, J.; Reynolds, J. R. "Soluble PheDOT Copolymers via Direct (Hetero)Arylation Polymerization: A Revived Monomer for Organic Electronics"
 3. Ponder, J.F.; Menon, A. K.; Dasari, R. R.; Pittelli, S. L.; Yee, S. K.; Marder, S R.; J. R. Reynolds "Electrical Conductivity Tuning via Structure and Processing of Soluble Dioxythiophene Copolymers"
- De Keersmaecker, M.; Lang, A. W.; Österholm, A. M.; Reynolds J. R. "An evaluation of conductive PEDOT:PSS electrodes in electrochemical devices"

PATENTS

US Patent: "Conjugated Polyelectrolytes as Water Processable Precursors to Organic and Aqueous Compatible Polymers for Charge Storage, Electrochemical and Bioelectronic Applications", Patent application 62/193,399.

DISSERTATIONS

Rayford H. Bulloch, PhD Dissertation “Redox-Active Conjugated Polymers for Electrochromic and Supercapacitive Applications”, July 2015

TECHNOLOGY TRANSFER

We have initiated a collaboration with the Naval Research Laboratory (Dr. Jeffery Long). An NDA has been put in place and polymers developed at Georgia Tech have been transferred to NRL for incorporation as anodes into asymmetrical supercapacitors. Results from this collaboration will be presented at the Electrochemical Society’s Fall Meeting in October, 2017 in Washington DC. Abstract entitled: “An Energy-Power Balancing Act: Balancing the High Capacity and Rate of LiMn_2O_4 -Carbon Nanofoam Cathodes with Solution-Processable Conducting Polymer Anodes”

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- (1) Shen, D. E.; Estrada, L. a.; Österholm, A. M.; Salazar, D. H.; Dyer, A. L.; Reynolds, J. R. *J. Mater. Chem. A* **2014**, 2 (20), 7509.
- (2) Österholm, A. M.; Shen, D. E.; Dyer, A. L.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2013**, 5 (24), 13432.
- (3) Liu, D. Y.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2010**, 2 (12), 3586.
- (4) Ponder, J. F.; Österholm, A. M.; Reynolds, J. R. *Macromolecules* **2016**, 49 (6).
- (5) Österholm, A. M.; Ponder, J. F.; Kerszulis, J. A.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2016**, 8 (21), 13492.
- (6) Ponder, J. F.; Pittelli, S. L.; Reynolds, J. R. *ACS Macro Lett.* **2016**, 5 (6), 714.
- (7) Ponder, J. F.; Österholm, A. M.; Reynolds, J. R. *Chem. Mater.* **2017**, 29 (10), 4385.